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Robert S. Burpo, Jr.

ATM	ATMOSPHERE
CAR	CARBON
FUR	FURNACE

CONTROL OF CARBON POTENTIAL

IN

FURNACE ATMOSPHERES

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Letter on cover:

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by

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PREFACE

The carburizing of low carbon steel as an industrial process has been practised for many years. Gradually this process has been refined and improved. Positive control of the amount of carbon added to the heated steel during the carburizing process has been the last of the techniques to be refined.

During World War II efforts were made to salvage quantities of aircraft parts that had undergone skin decarburization while being processed. The restoration of the missing carbon to the surfaces of the work-pieces was accomplished and carbon restoration has since become an important industrial process.

The theoretical basis that makes possible the accurate control of the carbon potential of a furnace atmosphere has been surveyed. The application of the theory developed herein makes possible the accurate carburizing and carbon restoration processes used so widely today.

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LIST OF SYMBOLS AND ABBREVIATIONS

(Fe,C)	Steel or iron-carbon alloy; this symbol may represent a solid solution of carbon in γ-iron or one of the polyphase forms of iron-carbon alloy depending on the carbon content and temperature.
(1)	Numbers appearing in brackets pertain to the references listed in the Bibliography appended to this paper.
1500F (816C)	Temperature in degrees Fahrenheit with its Centigrade equivalent in parentheses.
A_c	Activity of an element or compound usually used with a subscript denoting the particular element or compound.
P_{CO}	Partial pressure of a gas usually used with a subscript denoting the particular element or compound. eg $P_{CO} = pN_{CO}$ where p is the total pressure of the gas and N_{CO} is the mol fraction of CO.
K	Equilibrium constant.
R	An equilibrium ratio of gases.
Fe_α, Fe_γ	Alpha iron (bcc ferrite) and gamma iron (fcc austenite) respectively.
F	Free energy.
S	Entropy.
E	Internal energy.
R_o	Universal gas constant.

I

INTRODUCTION

1. Scope of This Paper

The heat treatment of iron and steel in controlled atmospheres is one of the important industrial processes of our modern technology. The development of the techniques, furnaces, atmosphere generators and of the control equipment has indeed been rapid during the past quarter century.

The use and understanding of furnace atmospheres with controllable carbon potentials is based on the application of certain principles of thermodynamics. Gibbs' phase rule and heterogeneous equilibria are two of these principles. Carburizing, carbon-restoration and neutral or "bright" hardening are three widely used processes and they all depend on the control of the carbon potential of their respective atmospheres. Of these, carbon-restoration is the newest process; it was introduced during World War II and it has been improved and refined during the post war years. This paper will survey the utilization of the phase rule as one of the principles of heterogeneous equilibria in the control of these three important metallurgical processes.

Intimately associated with any detailed study of carburizing is the phenomenon of diffusion (a rate process) and its effects will not be considered in this study. This paper is concerned primarily with the principles by which the carbon potential of an atmosphere can be controlled for useful purposes. The regulation of the amount of carbon available in a given atmosphere at the hot steel-gas interface is the topic to be studied. The diffusion of the carbon after its solution

in the steel, although of no less importance, is considered to be outside the scope of this present paper. Likewise, the interactions of such active gases as nitrogen (as typified by the newer carbonitriding or nicarbing process) in the furnace atmosphere are not considered.

2. Summary

The thermodynamic system composed of a multicomponent gas and the steel charge inside a heated furnace can be described by specifying the values of a series of independent variables; the magnitudes of the dependent variables of the system are thereby fixed. The application of Gibbs' phase rule to such a situation determines the number of the possible variables that must be independent. The choice of which individual variables will be the independent ones is based on a study of the particular system and of the applicable principles of heterogeneous equilibria. If the system can be specified unambiguously, then, given suitable control apparatus, it can be controlled. The simplifications introduced by both the phase rule and the use of the appropriate equilibrium constants make control of these systems practicable because they reduce a complicated quantity of independent variables to a single variable, the control of which governs the entire system.

II

FURNACE ATMOSPHERES - THEORY

1. Gaseous Constituents of Atmospheres

Inside a furnace used for the heat treatment of steel parts the following* reactions may occur:

$$Fe + H_2O \rightleftharpoons FeO + H_2 \quad (1)$$

$$Fe + CO_2 \rightleftharpoons FeO + CO \quad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3)$$

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO \quad (4)$$

$$Fe + CO + H_2 \rightleftharpoons (Fe,C) + H_2O \quad (5)$$

$$2CO + Fe \rightleftharpoons (Fe,C) + CO_2 \quad (6)$$

$$Fe + CH_4 \rightleftharpoons (Fe,C) + 2H_2 \quad (7)$$

$$2CO + O_2 \rightleftharpoons 2CO_2 \quad (8)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad (9)$$

Each of these reactions is reversible depending on the ambient conditions, and its direction is determined by the LeChatelier-Braun principle**. All of these reactions need not occur at the same time nor are each of these equally desirable or beneficial. Reactions (1) and (2) are symbolic of the formation of scale and, hence, often represent undesirable conditions. Carburizing and carbon restoration reactions involve mainly reactions (5), (6) and (7). Reactions (5) and (6) are the more important ones taking place within a furnace used for neutral hardening.

*These nine reactions are assumed to represent all those that might occur under normal operating conditions. If there were any additional ones, they would have to be included in the following analysis or it would be invalid without them.

**See any standard text on physical chemistry (such as reference 1, page 25) for a discussion of the LeChatelier-Braun principle.

An analysis of a furnace atmosphere containing eight or ten (or more) constituents and having these connected by five or six equilibrium reactions (that may proceed in either direction) can be complex and unwieldy. By the application of the principles of heterogeneous equilibria, simplifications can be made that enable metallurgists and metallurgical engineers to understand and to control furnace atmospheres with a minimum of effort.

The following, then, is a summary of the studies of and information regarding furnace atmospheres as applied to the practical heat treatment of iron and steel.

2. Carbon Potential

Basically, the problem is one of carbon concentration control in the heat treating furnace. The so-called inert atmospheres (for reheating for forging, for bright annealing, or for hardening) are only inert as long as they permit no carburizing nor decarburizing (as well as no scaling); in other words an inert atmosphere should be in equilibrium with the carbon concentration of the steel being treated. For carburizing, the primary function of the atmosphere is to increase the carbon concentration in the surface of the steel. And for carbon restoration (often accomplished along with heating for forging or for hardening) the desire is to restore the carbon concentration to its original value in the surface of the steel (the furnace atmosphere then must have a definite and controllable carbon potential). The carbon potential of a furnance atmosphere is its carburizing ability (or the concentration of carbon in steel with which the atmosphere will be in equilibrium).

3. Application of the Phase Rule

When steel is being heat treated in a controlled atmosphere furnace, there are a maximum of four phases present (unless scaling or carbon deposition - sooting - takes place; then there will be five or six phases in the system): (1) the gas, (2) ferrite, (3) austenite, (4) cementite. Since pearlite is the lamellar mixture of ferrite and cementite, and ledeburite is the cementite-austenite eutectic mixture, these are not separate phases.

The term "equilibrium" has been used several times previously and it is stated that Gibbs' phase rule is only applicable to equilibrium states. A piece of steel in a furnace under equilibrium conditions will undergo no net change in its carbon content, neither will it be oxidized nor reduced, and its temperature will remain constant.

Carburizing is not an equilibrium process (it is a rate process) for the surface carbon of the steel is increased in response to the carbon potential of the furnace atmosphere; at the same time carbon is diffusing inward along a surface-to-core gradient. Equilibrium conditions are established when the change in carbon concentration at the surface of the steel is zero. If a 0.20% C steel is being carburized in an atmosphere having a 1.2% carbon potential, the surface will acquire a case analyzing approximately 1.2% carbon and this carbon concentration will not change with time after equilibrium has been established. A neutral atmosphere is, theoretically, in equilibrium with the material being heated so that neither carburization nor decarburization, scaling (oxidizing) nor reduction takes place. And for carbon restoration, the steel being treated acquires a surface carbon concentration equal to that at the core (and the same as the original surface carbon concentra-

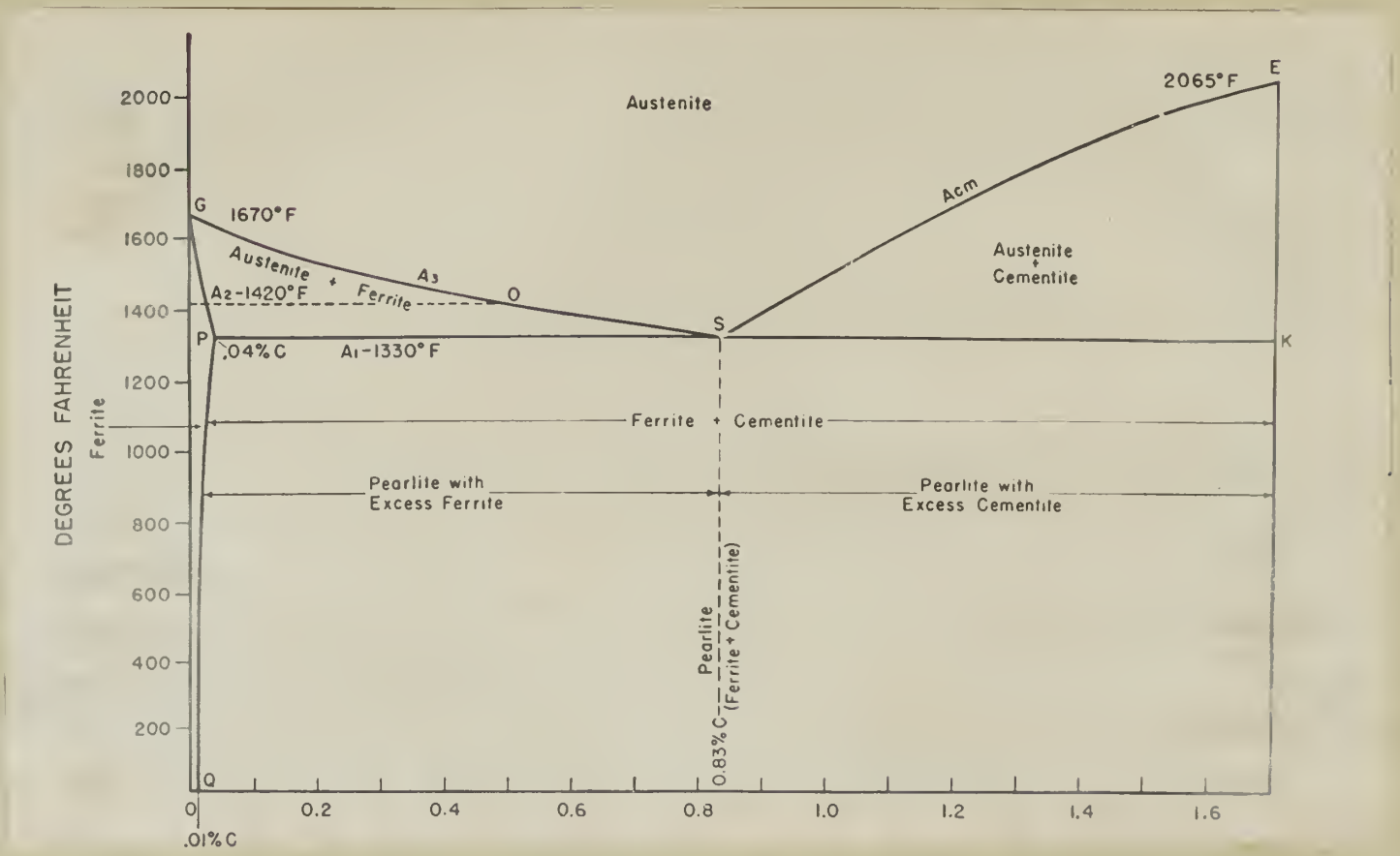

Fig. 1. Iron-Carbon Diagram. (14)

tion before decarburizing occurred). In this process the furnace atmosphere has a carbon potential equal to that of the steel prior to decarburization - and when equilibrium conditions occur within the furnace, the steel has been restored to its original carbon content and further time at temperature will not alter its analysis.

4. Analysis of a Simple Atmosphere

If steel were being treated in a furnace containing a simple atmosphere consisting solely of CO and CO_2, the reaction at the surface of the steel would be

$$Fe + 2CO \rightleftharpoons (Fe,C) + CO_2. \qquad (6)*$$

Let us assume that the concentration of CO in this atmosphere is high enough so that the reaction represented by equation (6) can only proceed to the right; i.e., no scaling takes place.

For the sake of concreteness, consider that the steel being treated is 0.50%C and that it is being heated at 1500F (816C). These data, then, determine the point on the iron-carbon diagram, Fig. 1, representing equilibrium conditions in the furnace. Obviously the variables needed to specify unambiguously the state of this system are:

1. The temperature of the system.
2. The pressure on the system.
3. The C:Fe ratio in austenite.
4. The $CO:CO_2$ ratio in the gas.

*Equation (6) is one (of many) symbolic ways of writing the over-all carburizing action. As a result of his tracer studies of the mechanism of carburizing, J. K. Stanley (1) uses this reaction, see also reference (4). It has been stated (2) that the carburizing reaction takes place in two stages: $2CO \rightleftharpoons CO_2 + C$ and $Fe + C \rightleftharpoons (Fe,C)$. When calculating the equilibrium constant for this process, the two subsidiary equation are added and their individual equilibrium constants are multiplied to find that for the overall reaction.

Reaction (6) describes a three-component system, and the iron-carbon diagram, Fig. 1., indicates that the particular process under discussion occurs in a two-phase (austenite-gas) area. With these two parameters known, Gibbs' phase rule can be employed to establish the number of independent variables which are required to specify the system unambiguously. The phase rule is summarized in equation (10):

$$V = A - B + 2 \qquad (10)$$

where V is the number of independent variables, A is the number of components in the system, and B is the number of phases. For the simple process being described A = 3, B = 2 and hence, V = 3. This means that any three of the four variables listed above can be selected as independent and the fourth is then fixed. If the temperature (1500F in this example), the pressure (commonly one atmosphere) and the carbon content of the steel (C:Fe ratio in austenite) are the three independent variables that can be selected to satisfy requirements, there is only one value of the $CO:CO_2$ ratio in the furnace atmosphere that will be in equilibrium with these conditions.

A different group of three independent variables could have been selected. Suppose that it was desired to carburize some steel parts at 1650F (890C) in this simple $CO-CO_2$ atmosphere. If the atmosphere composition were known (i.e., if the $CO:CO_2$ ratio were established), what carbon content would be found in the surface of the steel being treated? The independent variables would then be: temperature, pressure and the $CO:CO_2$ ratio. The equilibrium diagram (Fig. 1) will give the C:Fe equilibrium ratio that will be established in the steel (neglecting any diffusion effects) regardless of the time at temperature (as long as equilibrium conditions have been established) and independent of the

initial carbon content of the steel.

The equilibrium constant for the simplified atmosphere under discussion, reaction (6), can be expressed as

$$K_6 = \frac{A_c \, P_{co_2}}{A_{Fe} \, (P_{co})^2} \qquad (11a)$$

where P_{co} and P_{co_2} are, respectively, the partial pressures of CO and CO_2, A_{Fe} is the activity of austenite (and is equal to unity) and A_c is the activity of carbon in solid solution in the austenite. Equation (11a) can be rewritten as:

$$K_6 = A_c \frac{P_{co_2}}{(P_{co})^2} \qquad (11b)$$

A survey of the experimentally determined equilibrium constants of various gaseous reactions, including that of equation (6), is contained in a study made by J. B. Austin and M. J. Day (3). A graph showing the variation of the K_6 with temperature is plotted in Fig. C, Appendix. The changes in the activity of carbon (with respect to graphite as its standard state) for two different temperatures are graphed in Fig. B, also in the Appendix. Using the known values for A_c and K_6 and substituting them in equation (11b), the ratio of $CO:CO_2$ that will be in equilibrium with a given carbon content of steel (at a particular temperature) can be computed.

The foregoing analysis of the simple $CO:CO_2$ furnace atmosphere has been limited to one of the two 2-phase systems (the gas-austenite system).

From the viewpoint of the practical metallurgist the other two-phase system (ferrite-gas) is of slight practical importance except in the field of powder metallurgy and it will not be discussed here.

There are two three-phase systems of interest: the ferrite-austenite-gas, and the austenite-cementite-gas systems. Since little heat treating of the type involving carburizing, carbon restoration and/or hardening is performed below 1350F (733C), the three-phase system* existing below the $A_1 - A_{1,3}$ line (see Fig. 1) will not be discussed in this paper.

The study of the simple atmosphere $CO:CO_2$ as applied to the three-phase systems of interest leads to some valuable conclusions. Applying the phase rule, equation (10), to these systems:

$$V = A - B + 2 \qquad (10)$$

A = 3 (as in the previously discussed two-phase system), B = 3 and, therefore, V = 2. This means that of the four variables (temperature, pressure, C:Fe ratio, and $CO:CO_2$ ratio) two are independent. If the values for temperature and pressure are selected (i.e., if temperature and pressure are the independent variables) for the austenite-cementite-gas system, the carbon content (C:Fe ratio) of the austenite plus cementite is fixed as is the $CO:CO_2$ ratio that is in equilibrium with this. Now with the carbon content of the gross solid phase (austenite plus cementite) fixed, the proportion of austenite to cementite** is variable but not the carbon content of the austenite. The carbon content of the cementite is, of course, constant at 6.7% by virtue of its being the compound Fe_3C. Thus a large number of steel analyses (within the appropriate range on the iron-carbon diagram) are in equilibrium with one specific $CO:CO_2$ ratio at a particular temperature. This means that with the equilibrium $CO:CO_2$

*The ferrite-cementite-gas phase.

**When austenite and another solid phase coexist (in equilibrium), and the carbon content of one is established, that of the other is also fixed. At constant temperature, increasing or decreasing the amount of carbon in such a system merely increases or decreases the amount of the second phase present.

mixture, steels within the appropriate range of carbon content will neither be carburized nor decarburized whereas any other gas ratio will tend to either carburize the steel to 100% cementite or to decarburize it to the value of carbon represented by the intersection of the appropriate isotherm with the A_{cm} line.

Similarly the situation in the ferrite-austenite-gas area of the iron-carbon diagram is analogous. From equation (10) there are the same number of independent variables as in the previous three-phase case. And, likewise, at any given temperature one $CO:CO_2$ ratio is in equilibrium with a range of steel analyses. Any deviation from this equilibrium gas mixture will result (if sufficient time is allowed) in either carburizing to 100% cementite or in decarburizing to ferrite.

The only other area of the iron-carbon diagram within the range of interest in this paper is the $A_1 - A_{1,3}$ line - an invariant system. Most of the heat treating operations discussed in this paper take place at temperatures above this line, so that this case is of limited practical importance.

5. Analysis of a Complex Atmosphere

The foregoing discussion has been based on the assumption that a $CO:CO_2$ mixture was a possible furnace atmosphere. From an ecomonic standpoint such an atmosphere is impractical. In addition to CO and CO_2 the usual furnace atmosphere contains hydrogen, nitrogen, water vapor and, if carburizing is to be accomplished, methane (CH_4) may be present. A system consisting of steel and the gaseous constituents mentioned above is a five-component system. The variables needed to describe the system unambiguously are, then:

1. The temperature of the system.

2. The pressure on the system.

3. The C:Fe ratio in one of the solid phases.*

4. The CO percentage.

5. The CO_2 percentage.

6. The H_2 percentage.

7. The H_2O percentage.

8. The CH_4 percentage.

Since the inert gas nitrogen makes up the balance of the atmosphere, its percentage is determined by the relative quantities of other gases present. Exchanging the original simple gas, $CO:CO_2$, for a more complex one does not alter the number of phases present nor does it change the phase areas previously discussed.

Considering again the two-phase area of the iron-carbon diagram, Fig. 1, that is of practical importance: application of the phase rule, equation (10) yields A = 5 and B = 2; therefore, V = 5 so that there are five independent variables and three dependent variables needed to describe this complex-gas-steel system. The independent variables are usually chosen as the temperature, pressure, the C:Fe ratio in the austenite, the percent H_2 and the percent CO.** This leaves the values of CO_2, CH_4 and H_2O as dependent variables.

Within this complex gas atmosphere it is quite likely that all nine of the possible reactions listed in Table I can occur.

*See second footnote, page 10.

**Reactions (2), (6) and (8) indicate individually that either the percentage of CO or that of CO_2 (but not both) may be selected as an independent variable.

There are four independent equilibrium gas ratios and five dependent combinations, each of which must be established and maintained in the furnace if the carbon potential is to be controlled. The mutual interactions of the various gaseous constituents is complicated: there are five reactions in which CO_2 takes part (either as a reactant or as a product) and if any one of these five reactions can be considered to generate it independently, its presence would upset the equilibrium ratios of the other four reactions according to the Le Chatelier-Braun principle. Since each of the nine possible reactions influences one or more of the other concurrent reactions, the effect of one reaction alone cannot be isolated and changing the ratio of reactants to products in the case of one reaction may effect several other reactions. In summation, then: the two-phase system with a practical atmosphere is complicated by the number of variables that must be controlled if the desired results are to be obtained.

For the three-phase system (austenite-cementite-gas) with the complex gas the situation is likewise complicated. Application of the phase rule, equation (10), to this system leads to the conclusion that four of the variables are independent and a like number are dependent.* Referring again to the iron-carbon diagram, Fig. 1: only the temperature and pressure determine the C:Fe ratio in the austenite; the carbon content of the other solid phase (cementite) is constant. This means, then, that the C:Fe ratio in the austenite is a dependent variable just as it was in the case of the three-phase-simple-gas system. The phase rule allows four independent variables for this system; they are: temperature, pressure,

*$V = A - B + 2$, where $A = 5$, $B = 3$; and $V = 4$.

CO and H_2 percentages. Hence the dependent variables must be the percentages of CO_2, H_2O, CH_4 and the ratio of C:Fe in austenite. Similarly, for the other three-phase system of practical interest (the ferrite-austenite-gas system) the four independent variables are: temperature, pressure and the percentages of CO and H_2, the dependent variables being the C:Fe ratio, and the percentages of CO_2, H_2O, and CH_4.

The analyses of the other complex-gas-steel systems are not dealt with in this paper for, as was stated previously, they are of limited practical importance.

It might be well to summarize the lessons learned from the application of the phase rule to practical gas-steel-systems:

a. In the austenite-gas area of the iron-carbon diagram, there are five independent variables that must be governed if the steel-gas system is to remain under control. These variables may be - (1) temperature, (2) pressure, (3) the C:Fe ratio in the austenite, (4) H_2, and (5) CO. There are, then, three dependent variables: (1) CO_2, (2) CH_4, and (3) H_2O. For every steel composition that falls within this area on the iron-carbon diagram there is an equilibrium mixture of gases such that at the appropriate temperature the steel will neither be carburized nor decarburized (nor oxidized). In other words, it is theoretically possible to match the carbon potential of a furnace atmosphere to the carbon content of any steel falling within the austenite-gas area of the iron-carbon diagram. The control of the carbon potential of these atmospheres involves the maintenance of equilibrium conditions.

b. In the three-phase regions of the iron-carbon diagram, equilibrium gas mixtures can be found that will neither carburize, decarburize, nor oxidize the steel. However, these equilibrium gas mixtures are in-

dependent of the steel compositions. If a steel is treated in a non-equilibrium gas mixture (temperature and pressure only determine the equilibrium gas composition) the steel will either be carburized (to pure cementite), or decarburized (until its carbon content decreases to the value where the A_{cm} line and appropriate temperature ordinate intersect), depending on whether the carbon potential of the gas mixture is greater or less than that of an equilibrium mixture. In the three-phase regions there are four independent and four dependent variables that must be controlled. The independent variables may be: (1) temperature, (2) pressure, (3) CO, and (4) H_2; and the dependent quantities are (1) CO_2, (2) H_2O, (3) CH_4, and (4) the ratio of C:Fe in austenite.

TABLE I. EQUILIBRIUM CONSTANTS AND GAS RATIOS

REACTION NUMBER	EQUATION	EQUILIBRIUM CONSTANT	EQUILIBRIUM GAS RATIOS	REMARKS
1	$Fe + H_2O \rightleftharpoons FeO + H_2$	$K_1 = \frac{P_{H_2}}{P_{H_2O}}$	$R_1 = \frac{P_{H_2}}{P_{H_2O}}$	(Note 4)
2	$Fe + CO_2 \rightleftharpoons FeO + CO$	$K_2 = \frac{P_{CO}}{P_{CO_2}}$	$R_2 = \frac{P_{CO}}{P_{CO_2}}$	(Note 4)
3	$CO + H_2O \rightleftharpoons CO_2 + H_2$	$K_3 = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \frac{K_1}{K_2}$	$K_3 = \frac{R_1}{R_2}$	(Note 1)
4	$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$	$K_4 = \frac{(P_{CO})^2 (P_{H_2})^2}{P_{CO_2} P_{CH_4}}$	$R_3 = \frac{(P_{CO})^2}{P_{CO_2}}$, $R_4 = \frac{(P_{H_2})^2}{P_{CH_4}}$	
5	$Fe + CO + H_2 \rightleftharpoons (Fe,C) + H_2O$	$K_5 = A_c \frac{P_{H_2O}}{P_{H_2} P_{CO}}$	$K_5 = \frac{A_C}{R_1 P_{CO}}$	(Note 5)
6	$2CO + Fe \rightleftharpoons (Fe,C) + CO_2$	$K_6 = A_c \frac{P_{CO_2}}{(P_{CO})^2}$	$K_6 = \frac{A_C}{R_3}$	(Note 2)
7	$Fe + CH_4 \rightleftharpoons (Fe,C) + 2H_2$	$K_7 = A_c \frac{(P_{H_2})^2}{P_{CH_4}}$	$K_7 = A_c R_4$	(Note 3)
8	$2CO + O_2 \rightleftharpoons 2CO_2$	$K_8 = \frac{(P_{CO_2})^2}{(P_{CO})^2 P_{O_2}}$	$\frac{1}{K_8} = (R_2)^2 P_{O_2}$	
9	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$K_9 = \frac{P_{CH_4} P_{H_2O}}{P_{CO} (P_{H_2})^3}$	$\frac{1}{K_9} = R_1 R_4 P_{CO}$	

NOTES

1. $\text{Log } K_3 = \frac{3287}{T} - 1.650$ (T = Fahrenheit + 460) (17)

2. $\text{Log } K_6 = \frac{15970}{T} - 9.060$ (T = Fahrenheit + 460) (17)

3. $\text{Log } K_7 = -\frac{8370}{T} + 5.770$ (T = Fahrenheit + 460) (21)

4. When Fe and FeO are each in the solid state, the equilibrium constant is equal to the equilibrium ratio.

5. For a graph of the activities of carbon dissolved in iron, see Fig. B., Appendix.

III

THE CONTROL OF FURNACE ATMOSPHERES

From a practical viewpoint, the close control of each of the gaseous constituents in an atmosphere is not economically feasible. If the carbon potential of an atmosphere is to be maintained within close tolerances, positive control of all the independent variables (with equipment that is neither expensive nor bulky and that can be used by the average furnace operator) would be ideal. By applying the theory developed in Chapter II, it can be shown that elaborate and expensive equipment is not required for the precision control of the carbon potential in furnace atmospheres.

1. Commercial Atmospheres

For the heat treating operations discussed in this paper an endothermic gas generator is commonly used. The output of such a generator may be enriched with natural gas (largely methane), propane or butane if it is desired to increase the carbon potential of the atmosphere for carburizing.

The endothermic gas generator consists of: air-gas metering equipment, a catalyst filled reaction retort or cracking chamber, and a cooler. In essence, the operation of the generator proceeds as follows: the metering equipment forces an air-gas mixture of the proper proportion into the heated retort where the mixture is cracked to form a gas mixture containing no CO_2 nor excess CH_4. To prevent the hot gas (which contains CO) from reacting to form CO_2 and carbon, the cracked mixture is cooled rapidly to 600F. The theory of gas atmospheres and the details of their generation and control have been covered in several recent papers (8, 9,

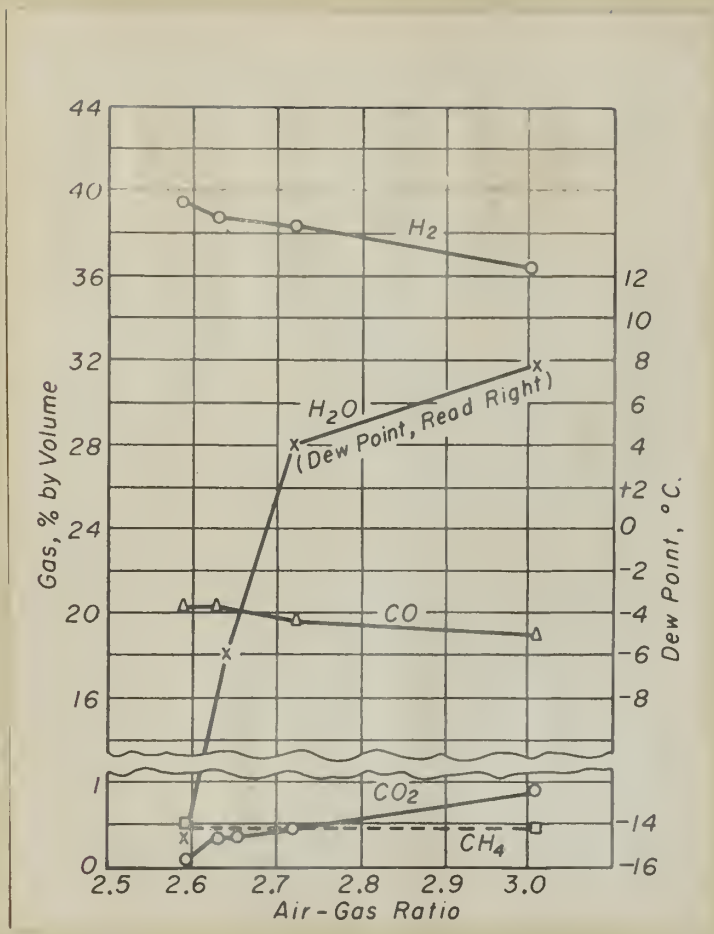

Fig. 2. Analysis of Product Atmosphere vs Changes in Input Air:Gas Ratio for Endothermic Gas Generator. (11)

10, 11, 12, 15 and 16).

A graph of the output of an endothermic atmosphere generator is shown in Fig. 2. Changes in the air-gas ratio fed into the generator alter the dew point, or water content, of the atmosphere far more than they effect the quantities of the other constituents. An average composition of endothermic gas would be:

CO: 20%

H_2: 40%

N_2: Bal.

The change in both H_2 and CO concentrations is very gradual (or, changes in the air-gas ratio produce much smaller changes in both the H_2 and CO contents).

2. Thermodynamic Basis for the Control of Atmospheres.

At this point it is well to summarize the predictions of the phase rule as to the independent and dependent variables for each of the areas of the iron carbon diagram discussed in Chapter I:

System	Independent Variables	Dependent Variables
Austenite - gas	Temperature, pressure, % C in austenite, CO and H_2.	CO_2, CH_4, H_2O
Austenite - cementite-gas and austenite-ferrite-gas	Temperature, pressure, CO and H_2	% C in austenite, CO_2, H_2O and CH_4

The relationships between the independent variables CO and H_2 and their corresponding dependent variables CO_2 and H_2O, respectively, are given by the pertinent equilibrium constants or equilibrium ratios (see Table I).

Since K_1 and R_1, are each determined by the temperature and pressure, fixing the value of P_{H_2} (by means of the control over the air-gas ratio) establishes the value of P_{H_2O} (which would be measured as dew point). Likewise, with the value of R_2 established by the temperature and pressure, and the percentage of CO established by the air-gas ratio selected, the value of P_{CO_2} is predetermined. Furthermore, reaction (3) has an equilibrium constant that is a function of R_1 and R_2 (showing that the H_2: H_2O ratio is related to the CO: CO_2 ratio by the relation $\frac{P_{H_2}}{P_{H_2O}} = K_3 \frac{P_{CO}}{P_{CO_2}}$).

Therefore, the dew point is a simple and suitable measure of the H_2: H_2O ratio as well as of the CO:CO_2 ratio. And the dew point can be readily changed by altering the air-gas ratio of the generator. See also Fig. 3.

Here, then, is the basis for the control of the heat treating atmosphere when it is in equilibrium with the steel being treated. The phase rule tells us how many variables must be controlled (as independent variables) and which ones are determined by the fixing of these (i. e. which ones are dependent). The relations between the particular pairs of variables and equilibrium ratios are established by applying the principles of heterogenous equilibria. Coupled with these is the ability to generate a controllable gas composed of predictable amounts of CO, H_2 and N_2. Thus, a means for controlling the carbon potential of a gaseous heat treating atmosphere has been demonstrated.

The control thus exercised via the dew point measurement and the air-gas ratio is applicable to a multicomponent gas. From a study of the interrelations of the equilibrium constants and ratios (shown in Table I)

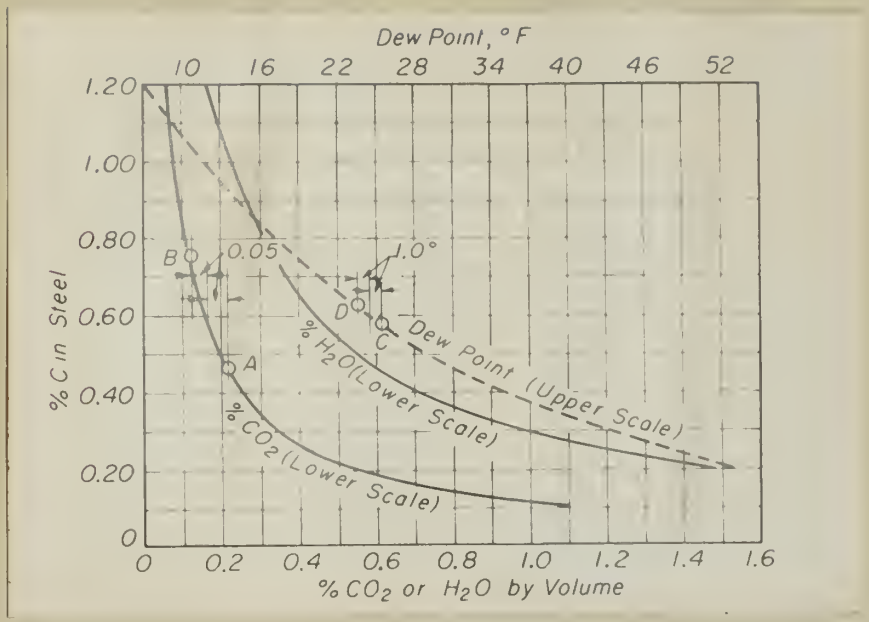

Fig. 3. Relation Between the Carbon Potential of an Endothermic Gas (20% CO, 40% H_2 and 40% N_2) at 1700F and the H_2O or CO_2 Content. Note that the dew point curve has a much flatter slope than that of the CO_2 curve and, then, a small error in the determination of the dew point does not lead to as large a variation in the carbon potential as does a similar error in the amount of CO_2. (15)

and figures (2) and (3) it can be seen that

> each value of $H_2O\%$ (or the dew point of the gas) may represent the value of the other dependent variables ($CO_2\%$ and $CH_4\%$) at equilibrium..... (7).

3. Control Equipment

Since most of the heat treating atmospheres are generated and used at a pressure slightly in excess of one atmosphere, no control of the pressure is needed. There are a wide range of temperature controlling devices, some recording, others indicating, and all capable of controlling furnace temperatures to within plus or minus two or three degrees. Dew-point measuring instruments of suitable accuracy are available for this type of work and cost from a few hundred dollars on up - depending upon the complexity of the instrument; automatic continuously recording instruments are, of course, more expensive than simple indicating instruments. As for the proportioning valves on the gas generator, these may be manual or automatic and are of standard types.

4. Carbon Potential Control in Practice

In Figure 4 are shown a series of equilibrium curves for some commonly used heat treating temperatures. These curves are the result of a series of practical tests. These have wide application; and, they are sometimes subject to misinterpretation. The curves of Fig. 4 represent equilibrium conditions - and they cannot be applied to other than equilibrium situations.

Remarks concerning the composition of gaseous atmospheres apply only to the atmospheres inside the furnace. The measurement of dew points must be made in the furnace (or in gases withdrawn from the furnace under isothermal conditions) and not at the generator.

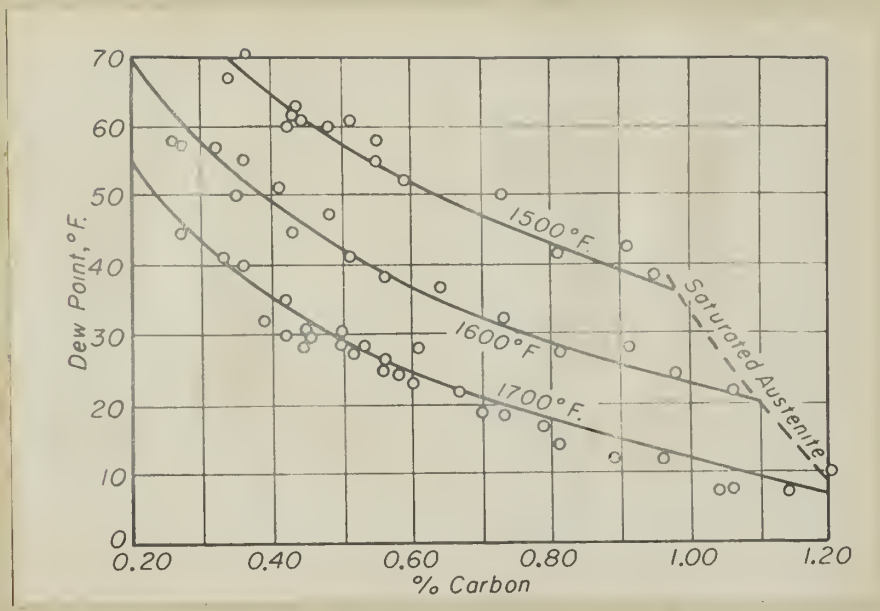

Fig. 4. Equilibrium Curves for Plain Carbon Steels in an Endothermic Furnace Atmosphere. (16)

5. Conclusion

In the last few years there has been an increasing industrial use of such equilibrium processes as "skin recovery" carburizing or carbon restoration, neutral hardening and controlled carburizing. Theoretically the complex equilibria found in a multicomponent gas atmosphere can be correlated and controlled through the application of the principles of heterogeneous equilibria. In practice it has found that the carbon potential of a complex-equilibrium-gas atmosphere (based on an endothermic carrier gas of constant percentages of CO and H_2 can be controlled by using its dew point as the control mechanism.

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APPENDIX I

SOME NOTES ON THERMODYNAMICS OF Fe-C SOLID SOLUTIONS

1. Ferrite-Austenite Equilibrium

On slow heating to a particular temperature (depending upon its carbon content - see Fig. 3) steel will change from ferrite (a body centered cubic lattice) to austenite (a face centered cubic lattice): $Fe_\alpha \rightleftharpoons Fe_\gamma$. At the equilibrium temperature this reaction will go sponteneously in the direction of decreasing free energy. The change in free energy for this transformation is

$$\Delta F^\circ = 110 - 3.65T \ln T + 0.00283T^2 + 21.3\ T$$

where T is measured in degrees Kelvin. (20)

Free energy may be defined as

$$F = E + PV - TS$$

and the change in free energy at constant temperature and pressure is

$$\Delta F = \Delta E - T\Delta S$$

where the change in the (PV) term can be neglected when dealing with solid-state systems.

On the slow cooling of austenite, either ferrite or cementite forms from the parent phase, depending upon its carbon content. Prior to the formation of either ferrite or austenite

> There is presumably an association between the iron and carbon atoms in the austenite that tends to lower the interaction energy (and hence the internal energy) by forming statistical groupings of carbon-rich and carbon-poor concentrations. At the same time the departure from randomness causes the entropy to decrease, and this acts to raise the free energy counter to the lowering effect of the internal energy term. The particular balance of internal energy and entropy which minimizes the free energy determines the distribution of concentrations characterizing the equilibrium state. (9)

At the equilibrium temperature where austenite and ferrite (or cementite) can coexist, the change in free energy with the change from Fe_α to Fe_γ, or vice versa, is zero.

The reaction $Fe_\alpha \rightleftharpoons Fe_\gamma$ has an equilibrium constant

$$K = A_\gamma / A_\alpha$$

where A_γ represents the activity of iron in austenite relative to its value in pure γ-iron and A_α represents that of iron in ferrite relative to its value in pure α-iron. Using this K the heat of transformation can be calculated, (4):

$$\Delta H = -R_o \frac{d(\ln K)}{d(1/T)}$$

A graph of some experimentally determined values for ΔH is given in Fig. A.

2. The Heat of Solution of Graphite in Austenite.

Smith gives the heat of solution of graphite in austenite as 9800 Cal. (4) and it can be calculated at any given temperature if the activity is known:

$$\Delta H_S = -4.575 \frac{d(\ln A)}{d(1/T)}$$

3. Solution of Carbon in Ferrite.

On the basis of a number of solubility experiments performed by Smith (4) and Pennington (5), the latter derived an equation for the saturated carbon content of ferrite:

$$C = 0.3936 - 0.000403\ F + 0.0000001F^2$$

where C is the percent carbon in the ferrite and F is the temperature.

4. Activity.

The subject of activity and its measurement (as well as its definition) seems to be one of a wide range of variation:

Birchenall and Mehl (6) define activity as $A = P/P^{o}$ where P is the partial pressure of the solute over the solution and P^{o} is the vapor pressure of the pure material in its standard state and at the same temperature. The activities of carbon in austenite calculated from Table 3 of Reference (6) are all less than unity. Pennington (5) defines activity in terms of concentration and states that when a solid solution of austenite is saturated with carbon the activity of the carbon is unity.

On the other hand, Stout and Toivo, on page 171 of the A.S.M. Symposium on Controlled Atmospheres, calculate an activity of carbon to be greater than unity. (1.15). Under these same conditions, Pennington (5) calculates the activity to be significantly less than unity.

It seems then, that the measured and computed values for the activity of carbon in both austenite and ferrite are a bit uncertain and that these cannot be used in practical computations - although the theoretical importance of activity is well understood.

An indication of the change in activity as a function of the carbon content of the steel is shown in Fig. B.

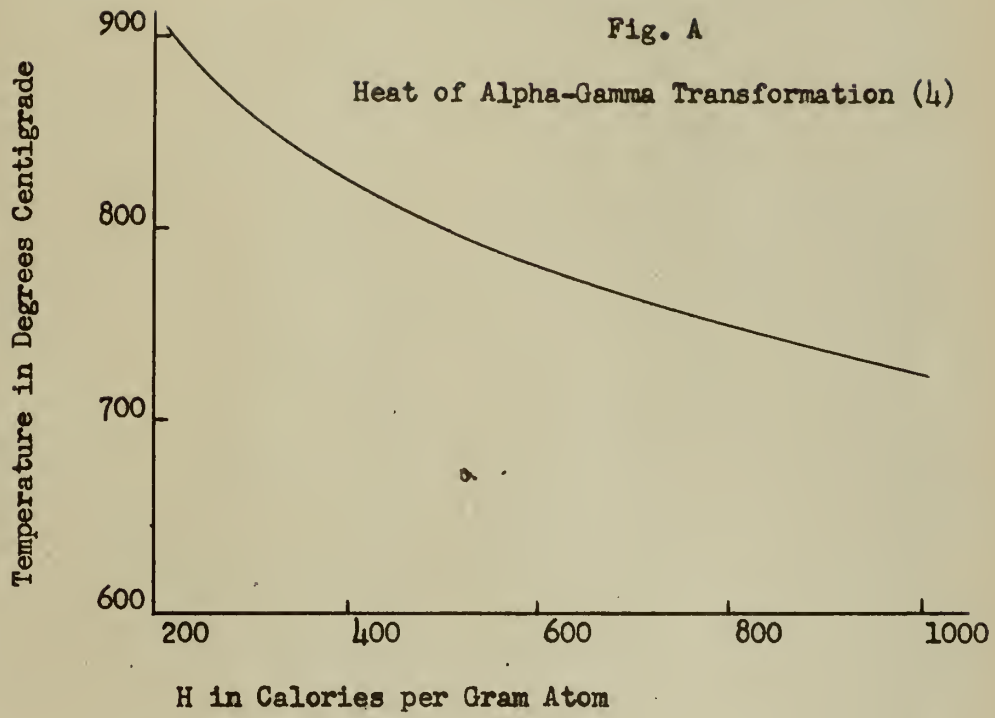
5. Variation in Equilibrium Constants

Several papers have appeared listing the values of some of the equilibrium constants that are of interest in controlled carbon potential processes. Fig. C shows how K_6 varies with temperature.

The values of equilibrium constants reported in the literature are more consistent than those of activities. Practical computations made with published values of equilibrium constants are reasonably reliable (providing the results of these computations are applied only to the interpretation of equilibrium systems). Because of variations in published values of carbon activities, the use of these in everyday metallurgical work is limited.

Fig. A

Heat of Alpha-Gamma Transformation (4)



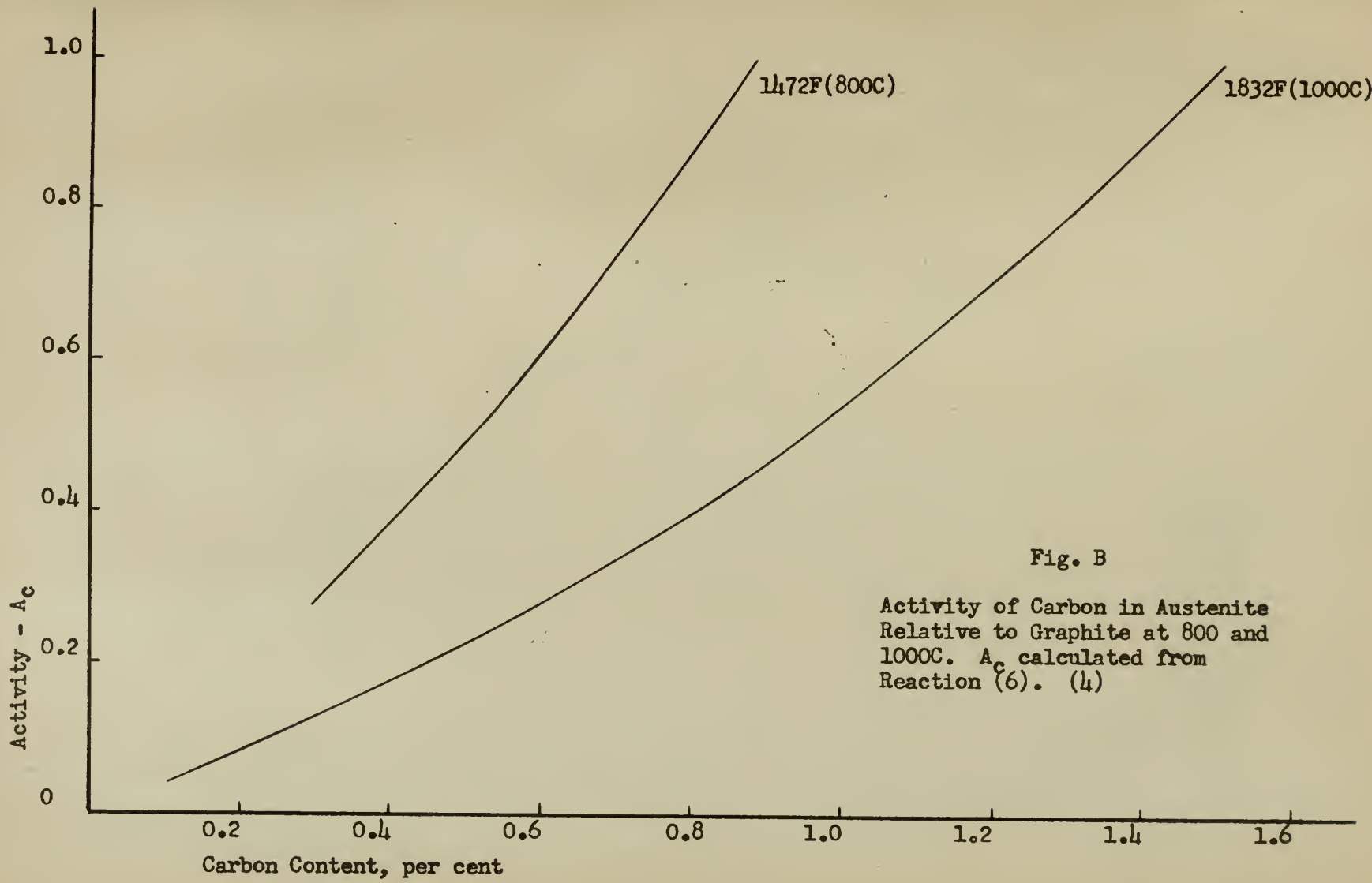


Fig. B

Activity of Carbon in Austenite Relative to Graphite at 800 and 1000C. A_c calculated from Reaction (6). (4)

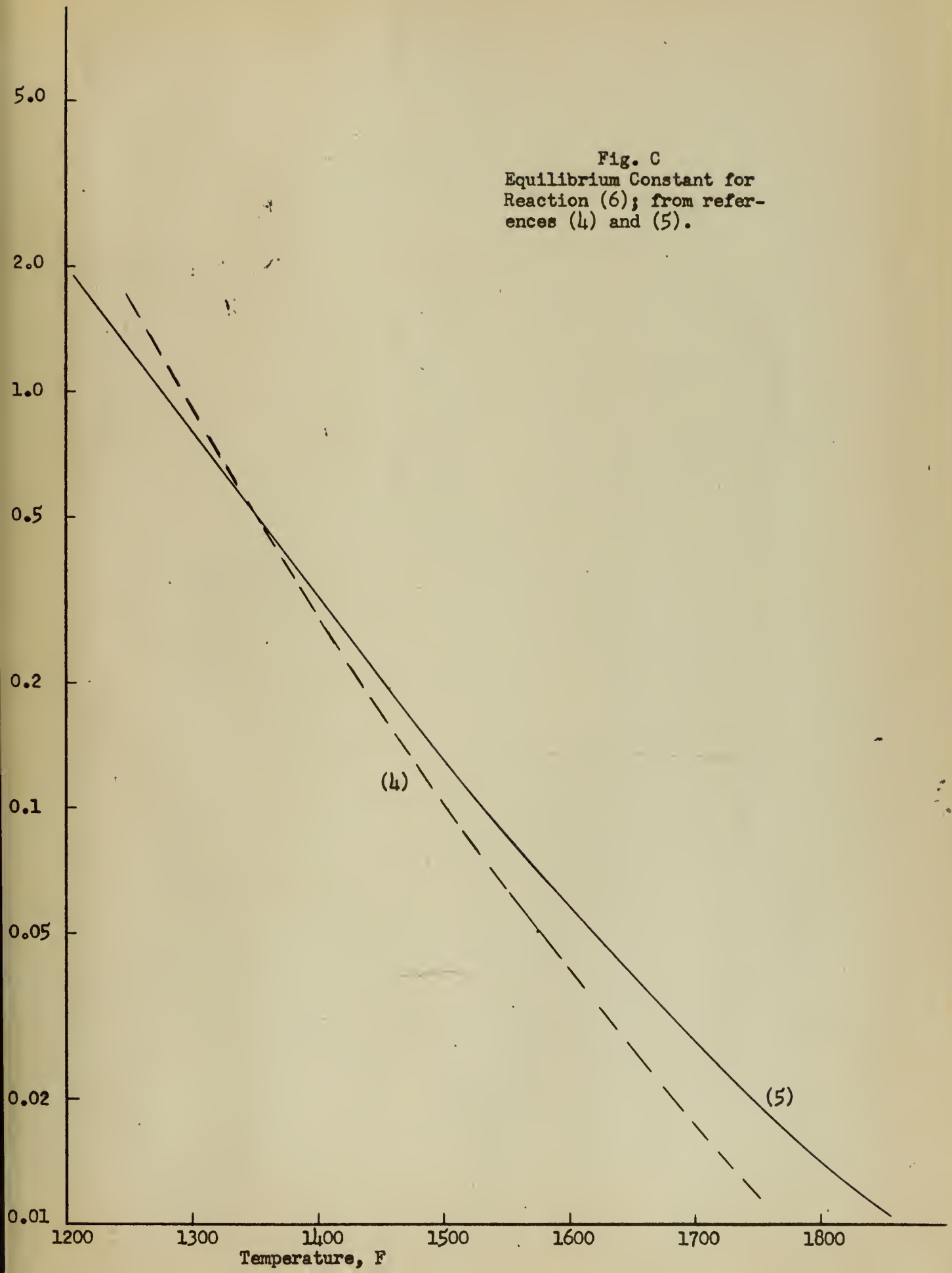
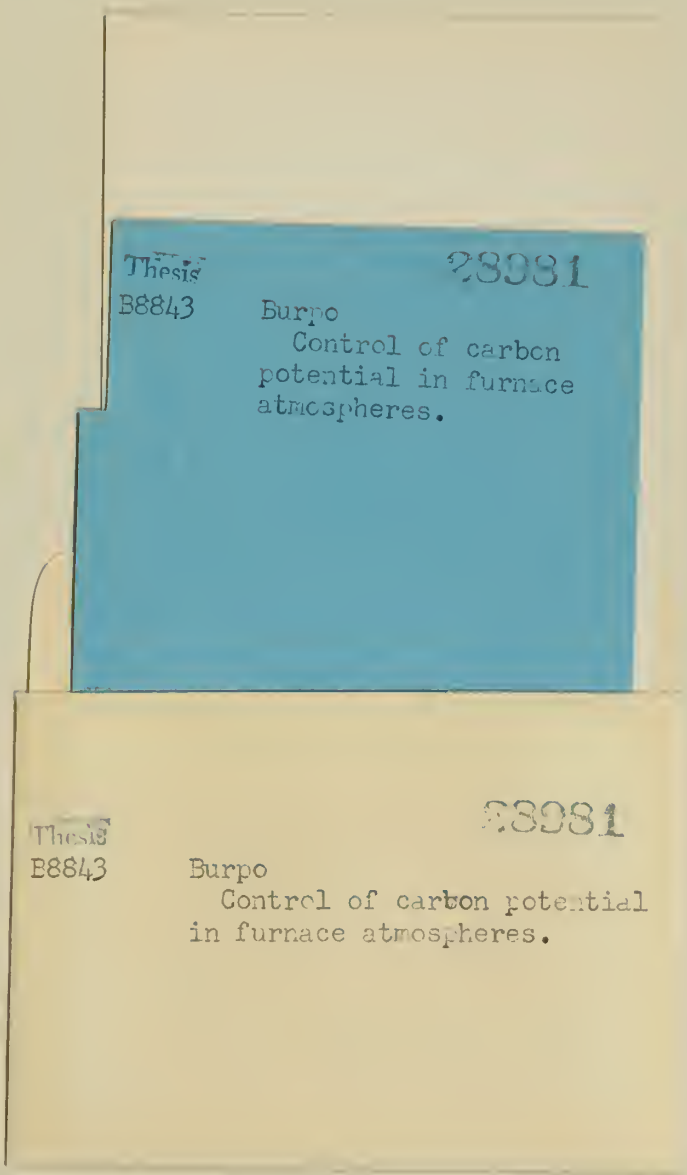


Fig. C
Equilibrium Constant for Reaction (6); from references (4) and (5).



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